

## RESEARCH ARTICLE

10.1002/2016JG003354

## Key Points:

- We assessed bulk N deposition and isotopes in urban and agricultural valleys
- N deposition and  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  were similar;  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  varied seasonally with land use
- Variable particulate N contributions may influence  $\delta^{15}\text{N}$  in bulk deposition

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## Citation:

Hall, S. J., E. M. Ogata, S. R. Weintraub, M. A. Baker, J. R. Ehleringer, C. I. Czimczik, and D. R. Bowling (2016), Convergence in nitrogen deposition and cryptic isotopic variation across urban and agricultural valleys in northern Utah, *J. Geophys. Res. Biogeosci.*, 121, 2340–2355, doi:10.1002/2016JG003354.

Received 26 JAN 2016

Accepted 23 AUG 2016

Accepted article online 25 AUG 2016

Published online 14 SEP 2016

## Convergence in nitrogen deposition and cryptic isotopic variation across urban and agricultural valleys in northern Utah

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**Abstract** The extent to which atmospheric nitrogen (N) deposition reflects land use differences and biogenic versus fossil fuel reactive N sources remains unclear yet represents a critical uncertainty in ecosystem N budgets. We compared N concentrations and isotopes in precipitation-event bulk (wet + dry) deposition across nearby valleys in northern Utah with contrasting land use (highly urban versus intensive agriculture/low-density urban). We predicted greater nitrate ( $\text{NO}_3^-$ ) versus ammonium ( $\text{NH}_4^+$ ) and higher  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in urban valley sites. Contrary to expectations, annual N deposition ( $3.5\text{--}5.1\text{ kg N ha}^{-1}\text{ yr}^{-1}$ ) and inorganic N concentrations were similar within and between valleys. Significant summertime decreases in  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  possibly reflected increasing biogenic emissions in the agricultural valley. Organic N was a relatively minor component of deposition ( $\sim 13\%$ ). Nearby paired wildland sites had similar bulk deposition N concentrations as the urban and agricultural sites. Weighted bulk deposition  $\delta^{15}\text{N}$  was similar to natural ecosystems ( $-0.6 \pm 0.7\%$ ). Fine atmospheric particulate matter ( $\text{PM}_{2.5}$ ) had consistently high values of bulk  $\delta^{15}\text{N}$  ( $15.6 \pm 1.4\%$ ),  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  ( $22.5 \pm 1.6\%$ ), and  $\text{NO}_3^-$  ( $8.8 \pm 0.7\%$ ), consistent with equilibrium fractionation with gaseous species. The  $\delta^{15}\text{N}$  in bulk deposition  $\text{NH}_4^+$  varied by more than 40‰, and spatial variation in  $\delta^{15}\text{N}$  within storms exceeded 10‰. Sporadically high values of  $\delta^{15}\text{N}$  were thus consistent with increased particulate N contributions as well as potential N source variation. Despite large differences in reactive N sources, urban and agricultural landscapes are not always strongly reflected in the composition and fluxes of local N deposition—an important consideration for regional-scale ecosystem models.

### 1. Introduction

Atmospheric nitrogen (N) deposition derived from anthropogenic sources represents a significant N input to most regions on Earth [Galloway *et al.*, 2004]. Estimating these fluxes and ascertaining their sources over local and regional scales is critical for assessing ecosystem impacts of N as well as for informing environmental policy and regulatory compliance. However, this endeavor is complicated by the presence of numerous biogenic and/or anthropogenic sources—especially agricultural emissions from animal waste or fertilized soils, fossil fuel combustion, and industrial emissions—that have heterogeneous spatial and temporal distributions. Monitoring the chemical composition of precipitation represents a potentially effective strategy for assessing spatial and temporal variations in atmospheric reactive N sources.

In the United States, the National Atmospheric Deposition Program (NADP) uses a network of precipitation sampling sites explicitly located away from urban centers to estimate wet deposition of N at the national scale [Bigelow *et al.*, 2001]. Avoiding urban areas implicitly assumes that local urban emissions impact the chemical composition of precipitation at a given urban site. It is generally assumed that urban areas dominate oxidized N emissions, while agricultural areas dominate reduced N emissions to the atmosphere [Hertel *et al.*, 2012]. However, the impacts and relative importance of urban and agricultural emission hot spots on the spatial and temporal distributions of N deposition remain understudied.

Discrepancies between estimated reactive N emissions and measured deposition fluxes suggest that existing sampling networks have undersampled N deposition associated with urban and agricultural emission hot

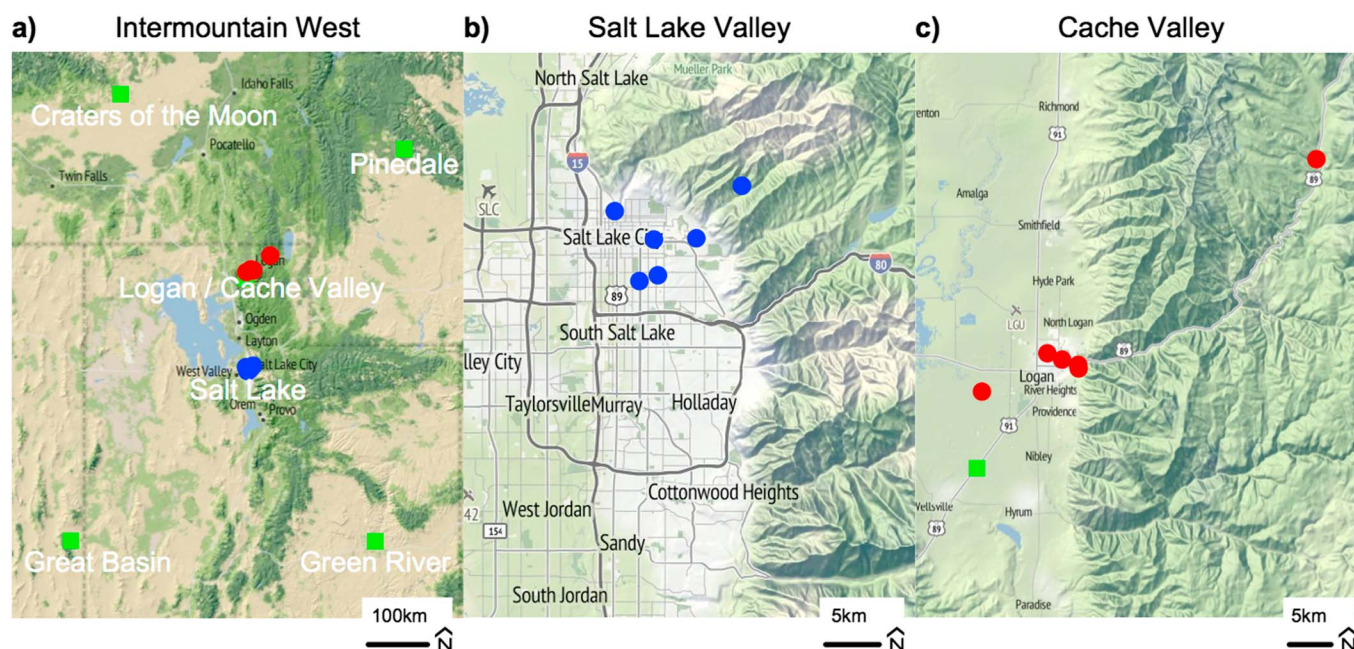
spots [Holland *et al.*, 2005]. Total N deposition is typically higher in urban versus wildland areas [Fenn and Bytnerowicz, 1997; Lovett *et al.*, 2000; Fang *et al.*, 2011; Bettez and Groffman, 2013; Rao *et al.*, 2014]. Fossil fuel combustion is concentrated in urban areas [Gurney *et al.*, 2009] and represents the dominant source of nitrogen oxides ( $\text{NO}_x$ ) to the atmosphere [Galloway *et al.*, 2004]. Most  $\text{NO}_x$  oxidizes to nitrate ( $\text{NO}_3^-$ ) within hours [Beirle *et al.*, 2011] and is subsequently removed by wet or dry deposition over time scales of minutes to days [Hertel *et al.*, 2012]. Several studies documented increased dry deposition and foliar N uptake adjacent to roads due to vehicular  $\text{NO}_x$  emissions [Ammann *et al.*, 1999; Pearson *et al.*, 2000; Redling *et al.*, 2013]. Fertilized agricultural soils also represent a major  $\text{NO}_x$  source, particularly in semiarid climates where low moisture enhances microbial NO production [Davidson and Kinglerlee, 1997; Hertel *et al.*, 2012]. The impacts of agricultural  $\text{NO}_x$  on  $\text{NO}_3^-$  deposition have received little attention in comparison with fossil fuel combustion.

Ammonium ( $\text{NH}_4^+$ ) in soluble and particulate forms, in equilibrium with gaseous  $\text{NH}_3$  emitted to the atmosphere, represents the other primary component of bulk N deposition. Together, these species ( $\text{NH}_x$ ) have typical atmospheric residence times of hours to days; particulate  $\text{NH}_4^+$  has lower dry deposition velocities and longer residence times [Hertel *et al.*, 2012]. Agricultural regions with intensive livestock production and fertilizer application are the primary source of global  $\text{NH}_3$  emissions [Galloway *et al.*, 2004]. However, urban areas increasingly represent a source of  $\text{NH}_3$  from vehicular fossil fuel combustion [Kean *et al.*, 2000] in addition to smaller sources from industry and other organic wastes (e.g., landfills and sewage treatment plants) [Battye *et al.*, 2003]. Organic N may contribute an important but highly variable component to total deposition [Cape *et al.*, 2011], although relationships between organic N and land use remain poorly characterized.

Despite the strong association between land use and emissions of  $\text{NO}_x$  and  $\text{NH}_3$  [Hertel *et al.*, 2012], relatively few studies have assessed impacts of intensive urban and agricultural land use on regional-scale (i.e., scales of tens to hundreds of kilometers) patterns of bulk N deposition [Lohse *et al.*, 2008; Tulloss and Cadenasso, 2015]. Previous studies often used forested urban to rural gradients, with natural or low-intensity agricultural landscapes as the end-member [Fenn and Bytnerowicz, 1997; Lovett *et al.*, 2000; Fang *et al.*, 2011; Bettez and Groffman, 2013; Rao *et al.*, 2014]. This work documented increased N deposition in proximity to urban centers, usually by measuring N inputs in throughfall from forested canopies. Plant canopies can more effectively scavenge atmospheric dry and fog deposition than a single planar surface (i.e., pavement or bare soil). The presence of a plant canopy typically increases deposition fluxes relative to “bulk deposition,” defined here as wet + dry deposition in the absence of overhanging plants [Fenn and Poth, 2004; Bettez and Groffman, 2013; Tulloss and Cadenasso, 2015]. Canopy throughfall deposition measurements clearly demonstrated the potential importance of urban areas as hot spots of dry N deposition.

Despite the useful information gained from throughfall deposition measurements, this method is less practical in heterogeneous urban and agricultural landscapes. First, plant species differ in their capacity to scavenge atmospheric N [Lovett, 1994; Fenn and Bytnerowicz, 1997; Sparks, 2009], which can confound assessments of land use impacts when vegetation covaries. Second, the deposition surface provided by a forest canopy is not necessarily representative of the broader landscape, especially in semiarid environments with few trees. Bulk deposition measurements provide a comparable metric for assessing regional differences in N deposition [Lewis *et al.*, 1984; Liu *et al.*, 2013], despite their underestimation of dry N deposition to canopies.

The stable isotope ( $\delta^{15}\text{N}$ ) compositions of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  complement measurements of N concentrations, potentially providing insights into spatial and temporal variations in reactive N sources to the atmosphere. Values of  $\delta^{15}\text{N}$  can reflect differences in sources and/or isotope fractionation during the production or emission of atmospheric reactive N. Atmospheric  $\text{NH}_3$  from biogenic sources such as urine and manure, and also inorganic fertilizer, often has low  $\delta^{15}\text{N}$  values (e.g.,  $-60$ – $0$ ‰ [Frank *et al.*, 2004; Skinner *et al.*, 2006; Felix *et al.*, 2013, 2014]) as a consequence of kinetic and equilibrium fractionation during  $\text{NH}_3$  volatilization. This isotopic variation arises both from  $\delta^{15}\text{N}$  values of the source of mineralized  $\text{NH}_3$ , as well as the extent of  $\text{NH}_3$  volatilization [Hogberg, 1997]. For example,  $\delta^{15}\text{N}$  values in animal waste and fertilizer vary between  $2$ – $25$ ‰ and  $-2$ – $2$ ‰, respectively [Bateman and Kelly, 2007; Kendall *et al.*, 2007], but can yield volatilized  $\text{NH}_3$  that is highly depleted in  $\delta^{15}\text{N}$ , e.g.,  $-56$  to  $-23$ ‰ [Felix *et al.*, 2013]. In contrast to biogenic or fertilizer sources,  $\text{NH}_3$  released or produced as a by-product of fossil fuel combustion may have relatively higher  $\delta^{15}\text{N}$  values, e.g.,  $-15$  to  $-2$ ‰ [Felix *et al.*, 2013], given that kinetic fractionation during a phase transition is less likely to be expressed. All else equal, greater values of  $\delta^{15}\text{N}$  of



**Figure 1.** Precipitation sampling locations in (a) the geographic context of the intermountain western United States, (b) the Salt Lake Valley, and (c) the Cache Valley. The green squares represent the NADP sites, and the blue and red circles are the sites sampled for the present study. This color scheme is continued in the following figures. The light-grey shaded areas of Figures 1b and 1c represent urban land use.

$\text{NH}_4^+$  in atmospheric deposition likely reflect greater contributions of combustion-derived  $\text{NH}_3$  relative to biogenic/fertilizer  $\text{NH}_3$ .

Variation in  $\delta^{15}\text{N}$  of  $\text{NO}_x$  and atmospheric  $\text{NO}_3^-$  has similarly been used to distinguish oxidized N contributions from fossil fuel and biogenic sources [Elliott et al., 2007; Walters et al., 2015]. Median values of  $\delta^{15}\text{N}$  of  $\text{NO}_x$  from coal combustion ( $\sim 10$ – $20\text{‰}$ ) are higher than median values of diesel and gasoline combustion ( $\sim -20$ – $5\text{‰}$ ), which are both higher than median soil  $\text{NO}_x$  ( $\sim -30\text{‰}$ ) [Li and Wang, 2008; Walters et al., 2015]. When comparing regions with similar fossil fuel  $\text{NO}_x$  sources, lower values of  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  likely reflect an increasing biogenic emission contribution. In contrast to  $\delta^{15}\text{N}$ , values of  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$  may be controlled by atmospheric conditions during  $\text{NO}_x$  oxidation and provide less insight into  $\text{NO}_x$  sources [Michalski et al., 2003].

The capacity of  $\delta^{15}\text{N}$  observations in bulk deposition to assess and record the influence of local emission sources on ecosystem N inputs remains largely unexplored. The origins of atmospheric  $\text{NH}_3$  and  $\text{NO}_3^-$  are of particular interest in the intermountain western United States because of their contribution to the formation of fine atmospheric particulate matter ( $\text{PM}_{2.5}$ ). In this region, winter cold air pools facilitate the accumulation of  $\text{PM}_{2.5}$  dominated by ammonium nitrate and ammonium sulfate, which represents a major public health concern and a significant N source [Mangelson et al., 1997; Malek et al., 2006; Kelly et al., 2013; Hall et al., 2014]. The isotopic compositions of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  could provide insight into their sources, i.e., from soil and biogenic processes versus fossil fuel combustion.

Here we collected bulk deposition samples on a precipitation-event basis at sites spanning two nearby montane valleys in northern Utah, USA, with contrasting land use: the highly urban Salt Lake Valley and the predominantly agricultural Cache Valley (Figure 1). Native vegetation is characterized by a patchwork of grasses, shrubs, and bare soil; urban landscapes support a discontinuous and variable canopy of street trees in a landscape dominated by pavement, lawns, and buildings; and agricultural areas consist of seasonal or irrigated pastures and row crops and bare soil for much of the year. We asked: do bulk N deposition, N speciation, or N isotope composition reflect land use differences within and between valleys and over time? We predicted that bulk deposition in the urban Salt Lake Valley would contain more  $\text{NO}_3^-$  relative to  $\text{NH}_4^+$  in deposition as a consequence of greater vehicular and industrial  $\text{NO}_x$  emissions in urban areas. We predicted that bulk deposition in the agricultural Cache Valley would have higher  $\text{NH}_4^+$  concentrations due to the

prevalence of cattle feedlots and fertilized fields (which volatilize  $\text{NH}_3$  that is deposited as  $\text{NH}_4^+$  in acidic precipitation) and lower local fossil fuel  $\text{NO}_x$  emissions. Similarly, we predicted that  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  would be higher in the Salt Lake Valley than in the Cache Valley due to increased fossil fuel versus biogenic/fertilizer sources. To provide further context, we compared bulk deposition N concentrations with wet deposition data from several regional NADP sites.

## 2. Materials and Methods

### 2.1. Study Area

The Salt Lake and Cache Valleys are characterized by a similar semiarid continental climate, with mean annual temperature of 11 and 9°C and annual precipitation of 410 and 500 mm, respectively, measured on the valley floors. Precipitation consists mostly of winter snow and spring and fall rains, punctuated by occasional summer storms. The Salt Lake Valley ( $\sim 25 \times 50 \text{ km}^2$ ) is a major metropolitan area with a human population > one million, whereas the Cache Valley ( $\sim 20 \times 60 \text{ km}^2$ ) is characterized by concentrated animal agriculture (cattle feedlots and dairies), pasture, and row crops and has similar populations of cattle and people (approximately 100,000 each or  $>100 \text{ km}^{-2}$ ; Utah State University Cooperative Extension, unpublished data). We assumed that measurements of atmospheric N deposition at sites in these valleys would reflect local (within-valley) emissions as well as an unknown regional contribution. There are no other major urban areas or hot spots of concentrated feedlots/agriculture within hundreds of kilometers of these valleys. In the Salt Lake Valley, within-valley fossil fuel combustion, and dilution and mixing with incoming cleaner air masses, can explain the majority of the temporal variation in carbon dioxide ( $\text{CO}_2$ ) concentrations [Strong *et al.*, 2011]. This finding implies that local (as opposed to regional) emissions might also be strongly linked to atmospheric reactive N concentrations in these valleys, especially given the shorter residence times of reactive N relative to  $\text{CO}_2$ . Montane valleys are an especially useful spatial scale of analysis in this region during winter, where temperature inversions allow mixing of local atmospheric emissions throughout the valleys over time scales of hours to days [Pataki *et al.*, 2005].

In each valley, site locations were chosen to characterize atmospheric inputs to intensively monitored watersheds in the iUTAH hydrologic observatory ([www.iUTAHepscor.org](http://www.iUTAHepscor.org)). Salt Lake Valley sites ( $n = 6$ ) were located within or adjacent to the Red Butte Creek watershed, a focal iUTAH watershed. Five of these sites were located in urban Salt Lake City and one in Red Butte Canyon Research Natural Area, an adjacent protected area (Figure 1b). Cache Valley sites ( $n = 5$ ) were located within the Logan River watershed, another iUTAH focal area. Three sites were located in the City of Logan (population  $\sim 50,000$ ), one along a roadside in an agricultural landscape with pasture and row crops, and another in Logan River Canyon east of the Cache Valley. We predicted that the deposition sampled in the urban Cache Valley sites would also reflect emissions from the adjacent agricultural landscape, which stretched for 20–30 km to the south, west, and north of Logan. In both valleys, urban sampling sites were located in fenced properties to prevent tampering with equipment. Two Cache Valley urban sites were relocated to nearby locations in April 2014 due to logistical constraints.

In Salt Lake City and the City of Logan, the tree canopy consisted largely of deciduous species native to the eastern United States and represented a relatively small portion of total land cover ( $\sim 26\%$ ) [Nowak *et al.*, 1996]. The wildland sites sampled here had similarly sparse tree cover and were dominated by low-statured ( $<1 \text{ m}$ ) herbaceous vegetation and shrubs. The agricultural Logan Valley sites were characterized by annual row crops and pasture.

### 2.2. Precipitation Sampling

Snow and rain samples in the Salt Lake Valley were collected on a precipitation event basis, whenever possible, from December 2013 to February 2015 (total  $n = 324$  samples). Samples were collected within 36 h of the end of precipitation events. In cases where samples could not be collected within this interval, samples were discarded and a clean collection bottle was installed to minimize the potential for microbial N immobilization. In the Cache Valley, snow and rain samples were collected from December 2013 to February 2014 and from April 2014 to February 2015 (total  $n = 168$  samples). Snow was collected from acid-washed high-density polyethylene (HDPE) surfaces mounted on storm boards using acid-washed polyvinylchloride cores as described by Hall *et al.* [2014]. Rain was collected in HDPE funnels (20 cm diameter) mounted 1 m above the ground on steel posts, installed away from overhanging vegetation. Funnels were



connected via Tygon tubing to HDPE bottles placed inside plastic cylinders buried beneath the soil. Funnel necks were plugged with polyester fiber to reduce infiltration of debris and replaced following rainfall events. Samples from March 2014 often represented a mixture of snow and rain and were separately collected in acid-washed HDPE buckets (18.9 L). After collection, samples were weighed to calculate precipitation amount, filtered through precombusted Whatman GF/F filters, and frozen until analysis. Daily time series of precipitation amount were obtained from rain gauges on the University of Utah and Utah State University campuses. Values of pH measured on a subset of samples were  $<6$ , indicating that  $\text{NH}_3$  volatilization was minimal.

Precipitation samples represented bulk (i.e., wet + dry) deposition, given that funnel and storm board surfaces were exposed to the atmosphere between precipitation events. Our protocol contrasted with precipitation sampling at National Atmospheric Deposition Program (NADP) National Trends Network sites, where containers were exposed to the atmosphere only during precipitation events using an automated sampler. To further investigate dry deposition contributions to bulk ion loading at our sampling sites, we rinsed the funnel collectors with 18.2 M $\Omega$  deionized water for ion analysis after periods of more than 2 weeks without rain. Given that there were only three such events during the study period, we added the ion fluxes from rinsed samples to ion loads from the subsequent precipitation event for ease of interpretation.

We also compared our observations with five nearby (i.e., within several hundred of kilometers) NADP sites in the intermountain western United States (Figure 1a): Pinedale, WY; Craters of the Moon National Monument, ID; Great Basin National Park, NV; Green River, UT; and Logan, UT. The Logan NADP site was 10 km southwest of our Logan collection sites, in close proximity ( $<100$  m) to animal feedlots. Samples from NADP sites were collected over weekly intervals according to protocols detailed in the National Trends Network operations manual ([http://nadp.sws.uiuc.edu/cal/PDF/NTN\\_Operations\\_Manual\\_v\\_2-2.pdf](http://nadp.sws.uiuc.edu/cal/PDF/NTN_Operations_Manual_v_2-2.pdf)). We analyzed the data corresponding to our period of sample collection (detailed above).

### 2.3. Chemical and Isotope Analyses

All samples were analyzed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations by ion chromatography (Metrohm Compact IC, Riverview, FL). Analytical precision of ion measurements was assessed using the relative standard deviations of certified standards analyzed as unknowns. Cumulative relative standard deviations of these standards measured  $<3\%$ . Mean-reported values of National Institute of Standards and Technology (NIST)-traceable certified standards differed by  $<4\%$  from measured values calculated using a separate set of NIST-traceable standards. Total dissolved N concentrations were measured on a subset of samples ( $n = 45$ ) with a Shimadzu TOC-V analyzer (Columbia, MD). Dissolved organic N (DON) was calculated as the difference between total dissolved N and inorganic N ( $\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$ ;  $\text{NO}_2^-$  was typically below detection limit and not discussed further). This approach occasionally yielded negative values ( $n = 6$ ), likely due to compounding analytical variability in the three separate chemical determinations ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and total dissolved N). The most negative DON sample measured  $-0.11 \text{ mg L}^{-1}$ ; thus, we assigned all samples with DON absolute values  $<0.11 \text{ mg L}^{-1}$  to zero to avoid positively biasing our results, as opposed to simply removing negative values.

A subset of precipitation samples ( $n = 162$ ) was analyzed for N isotope ratios ( $\delta^{15}\text{N}$ ) of  $\text{NH}_4^+$  using an  $\text{NH}_3$  diffusion method modified from Holmes *et al.* [1998]. Briefly, 30 mL of sample was added to a 60 mL HDPE bottle along with 1.5 g NaCl (to decrease the osmotic potential of the solution). A glass-fiber filter acidified with 30  $\mu\text{L}$  of 4 M  $\text{H}_3\text{PO}_4$  was sandwiched between Teflon tape and added to the bottle. Then, 90 mg of magnesium oxide was added to volatilize  $\text{NH}_3$ , and the bottle was immediately capped and incubated for 7 days on an orbital shaker/incubator at  $40^\circ\text{C}$  to allow  $\text{NH}_3$  to be completely trapped as  $\text{NH}_4^+$  on the acidified filter. Filters were analyzed for  $\delta^{15}\text{N}$  values (precision  $<0.2\text{‰}$ ) by combustion on an elemental analyzer coupled to an isotope ratio mass spectrometer (Finnigan MAT Delta S, San Jose, CA) at the Stable Isotope Ratio Facility for Environmental Research Facility at the University of Utah (<http://sirfer.utah.edu>). To verify a lack of fractionation during recovery of  $\text{NH}_4^+$  on filter disks, we also similarly analyzed ammonium sulfate solutions with known  $\delta^{15}\text{N}$  values. We obtained equivalent  $\delta^{15}\text{N}$  values (within  $0.2\text{‰}$ ) after diffusion of these standards.

Additionally, we analyzed a subset of precipitation samples ( $n = 53$ ) for  $\text{NO}_3^-$  isotopic composition ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) using *Pseudomonas aureofaciens* and the denitrifier method [Casciotti *et al.*, 2002] to generate  $\text{N}_2\text{O}$  for analysis on an isotope ratio mass spectrometer. We used U.S. Geological Survey (USGS) 32 and 34 reference materials (for  $\delta^{15}\text{N}$ ) and USGS 34 and 35 (for  $\delta^{18}\text{O}$ ) to express the data in  $\delta$  notation relative to atmospheric  $\text{N}_2$

and Vienna SMOW for N and O, respectively. Mean accuracy was 0.34‰ for  $\delta^{15}\text{N}$  and 0.39‰ for  $\delta^{18}\text{O}$ , assessed by comparing the difference between measured versus known values of USGS 35 (for  $\delta^{15}\text{N}$ ) and USGS 32 (for  $\delta^{18}\text{O}$ ) analyzed as unknowns. Sample precision, determined by standard deviations of several samples analyzed in triplicate, was 0.08‰ for  $\delta^{15}\text{N}$  and 0.26‰ for  $\delta^{18}\text{O}$ .

### 2.3.1. Nitrogen Isotope Ratios of $\text{PM}_{2.5}$

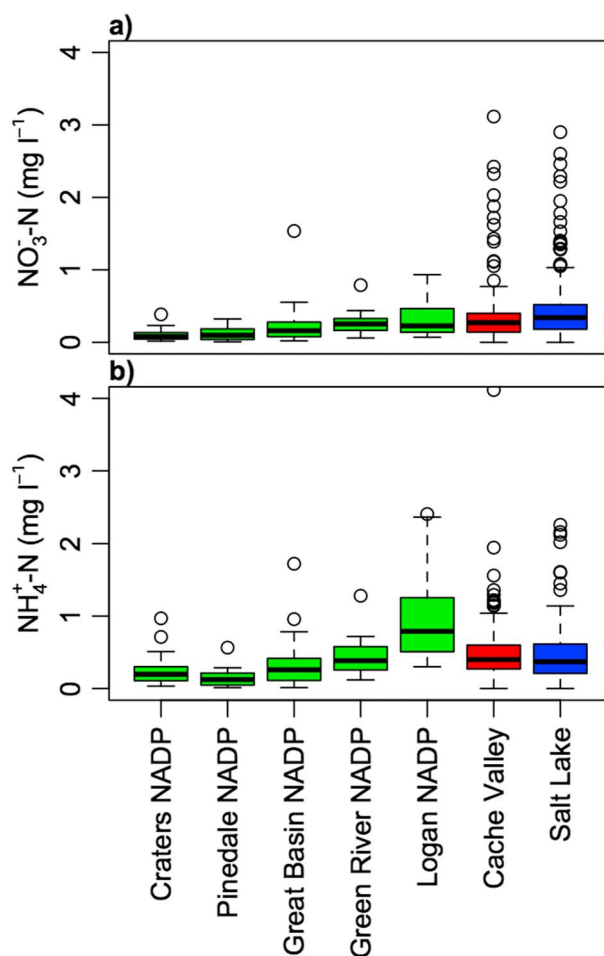
We sampled  $\text{PM}_{2.5}$  between January and February of 2015 at sites in urban Salt Lake City and near Logan, UT (in the Cache Valley), using calibrated high-volume air samplers at Utah Department of Air Quality (DAQ) sampling stations. Samples were collected over 2–5 day intervals, for a total of six Salt Lake City samples and four Logan samples. Salt Lake City samples were collected on 20 cm  $\times$  25 cm quartz microfiber filters (2500 QAT-UP, Pallflex Tissuquartz, Port Washington, NY). A subset of Salt Lake City samples and the Logan samples were collected on Teflon filters on DAQ-operated  $\text{PM}_{2.5}$  samplers. Comparisons of  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  extracted from quartz and Teflon filters sampled in Salt Lake City (see details below) showed no significant differences. Prior to sampling, quartz filters were precombusted at 500°C for 4 h and stored in aluminum foil inside sealed plastic bags. Blank filters were co-located inside aerosol samplers but not exposed to gas flow. During  $\text{PM}_{2.5}$  sampling, larger particles were removed with slotted microquartz fiber filters (TE-230-QZ, microquartz-slotted collection substrates, Tisch Environmental, Cleves, OH) on SA-230-F impactor plates (TE-230-QZ, Tisch). After collection, filters and blanks were wrapped in aluminum foil, packed into airtight plastic bags, and stored at  $-20^\circ\text{C}$ . For isotope analysis of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ , filters were immersed for 24 h in deionized water and solutions were filtered to 0.45  $\mu\text{m}$ . Values of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  were determined by the denitrifier method and  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  via diffusion as described above.

Bulk  $\text{PM}_{2.5}$  subsamples collected on quartz filters were also analyzed for total N content and  $\delta^{15}\text{N}$  with an elemental analyzer (NA 1500 NC, Thermo Scientific, Waltham, MA) coupled to an isotope ratio mass spectrometer (DeltaPlus, Thermo Fisher Scientific (Finnigan), Waltham, MA) at the Keck Carbon Cycle Accelerator Mass Spectrometry Facility of University of California, Irvine. Data were corrected for the N mass ( $1.4 \mu\text{g}/\text{cm}^2$ ) and  $\delta^{15}\text{N}$  ratios ( $-6.8\%$ ) of field blanks by isotope mass balance.

### 2.4. Data Analysis

We compared bulk ion concentrations between the Salt Lake and Cache Valleys using mixed-effect models, where sampling sites were treated as random effects to account for temporal autocorrelations. We separately tested for differences among sites in each valley using analysis of variance (ANOVA). We also binned the data into two seasons (November–March and April–October) to allow for seasonal comparisons between valleys while minimizing excessive post hoc comparisons over finer time scales (i.e., comparing all months). The latter time period represents the predominant growing season in our study area. We did not statistically compare our samples with NADP data given that they represent two different sample types (i.e., bulk versus wet deposition) but rather report NADP data for heuristic comparisons. We assessed cumulative bulk N deposition for 2014 as the product of precipitation amount and measured N concentrations at our sites; missing values from a particular site were replaced by the means for each event in each valley. We did not have a complete record of bulk deposition chemical composition in the Cache Valley sites from mid-February to early April 2014. Total bulk deposition N concentrations were statistically equivalent between valleys during the rest of our observation period (December 2013 to February 2015). Therefore, we estimated cumulative bulk N loading for Cache Valley sites during the period of missing data as the product of precipitation amount measured at Utah State University in Logan and mean N concentrations measured during this period in the Salt Lake Valley. Gap-filled data were not used in statistical tests comparing sites or valleys.

We assessed temporal trends in precipitation ion concentrations during 2014 using generalized additive models (GAMs) with a Gaussian link function, fitted using the *mgcv* package in R [Wood, 2006]. This method allowed us to test for significant seasonal patterns and also to test whether the two valleys had significantly different temporal patterns in N concentrations or  $\delta^{15}\text{N}$ —i.e., whether including a separate trend for each valley or site was statistically optimal. We fit ion concentrations as a smooth function of time using regression splines that were penalized according to their “wiggleness” during model fitting to achieve a statistically optimum degree of curvature. Curvature was expressed in terms of degrees of freedom (d.f.) analogous to the order of a polynomial, allowing for fractional d.f. The need to include differing smooth functions of time for different groups of sites (i.e., Salt Lake Valley, Cache Valley, and NADP sites) was assessed by comparing model Akaike information criterion.



**Figure 2.** Concentrations of (a)  $\text{NO}_3^-$  and (b)  $\text{NH}_4^+$  in weekly precipitation samples (NADP sites; green boxes) and event-based bulk deposition samples (Salt Lake and Cache sites from this study; red and blue boxes, respectively). Sites are ordered by increasing mean  $\text{NO}_3^-$  concentrations from left to right. The boxes represent the medians and the interquartile range, and data  $>1.5$  times the range from the box to the whiskers are denoted as outliers (circles).

Green River NADP site ( $\text{NO}_3^- = 0.34, 0.27, \text{ and } 0.25 \text{ mg NL}^{-1}$  and  $\text{NH}_4^+ = 0.37, 0.40, \text{ and } 0.38 \text{ mg NL}^{-1}$ , respectively; Figure 2). The Green River site was located 250–300 km southeast of these valleys in a relatively small town ( $\sim 1000$  people). Together, these data suggest regional congruence of bulk deposition N inputs to these northern Utah valleys as well as the nearby landscape, which were dominated by the wet deposition component.

However, median bulk deposition N concentrations at the Salt Lake and Cache Valley sites greatly exceeded wet deposition concentrations at several other more remote NADP sites in the region (Figure 2). This contrast supports the importance of local emissions in driving N deposition to the Salt Lake and Cache Valley sites, with impacts that declined with distance. Salt Lake and Cache Valley bulk deposition inorganic N concentrations exceeded wet deposition concentrations at the Great Basin NADP site ( $0.16$  and  $0.26 \text{ mg NL}^{-1}$  for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , respectively; Figure 2) and were more than twofold greater than the Pinedale and Craters of the Moon NADP sites ( $\text{NO}_3^- = 0.10$  and  $0.08 \text{ mg NL}^{-1}$  and  $\text{NH}_4^+ = 0.12$  and  $0.20$ , respectively; Figure 2). In contrast to the remote NADP sites, median  $\text{NO}_3^-$  concentrations at the Logan NADP site (located in the Cache Valley) were only slightly lower ( $0.23 \text{ mg NL}^{-1}$ ) than the bulk deposition values measured at the nearby sites sampled in this study ( $0.27 \text{ mg NL}^{-1}$ ), despite the fact that they only reflected wet deposition. This finding suggests a relatively minor year-round contribution of dry deposition to the bulk deposition fluxes that we measured, which

### 3. Results and Discussion

#### 3.1. Spatial and Temporal Patterns in Bulk Deposition Inorganic N Concentrations

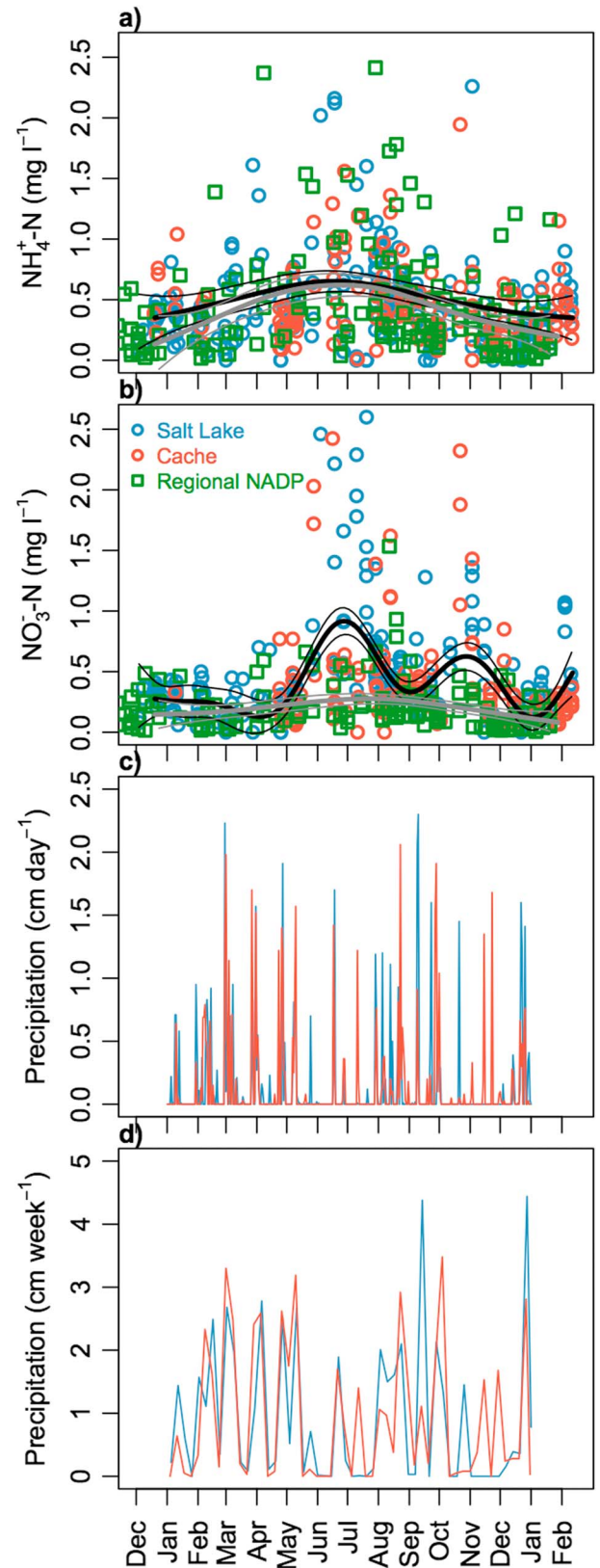
Contrary to our hypothesis that differences in urban versus agricultural land use would affect total bulk N deposition and speciation, fluxes and concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  did not significantly differ between Salt Lake and Cache Valley sampling sites on an annual basis (Figure 2). Ammonium concentrations in bulk deposition at the Salt Lake and Cache Valley sites were  $0.45 \pm 0.02$  and  $0.51 \pm 0.04 \text{ mg NL}^{-1}$  (means and standard errors), respectively, and  $\text{NO}_3^-$  concentrations were  $0.45 \pm 0.03$  and  $0.39 \pm 0.04 \text{ mg NL}^{-1}$ , respectively (Figure 2). However, bulk deposition  $\text{NO}_3^-$  concentrations (but not  $\text{NH}_4^+$ ) differed seasonally between valleys. During the growing season (April–October),  $\text{NO}_3^-$  was significantly greater at the Salt Lake ( $0.65 \pm 0.10 \text{ mg NL}^{-1}$ ) than the Cache Valley ( $0.42 \pm 0.08 \text{ mg NL}^{-1}$ ) sites ( $p < 0.01$ ). This pattern was predominantly driven by a peak in  $\text{NO}_3^-$  at the Salt Lake sites during June and July that was not observed at the Cache Valley sites (Figure 3).

Overall, concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  did not significantly differ among sites in a given valley, despite the inclusion of paired wildland sites (ANOVA,  $p > 0.05$ ). Median N concentrations in bulk deposition at the Salt Lake and Cache Valley sites were also of similar magnitude to median wet deposition N concentrations at the

excluded the influence of plant canopies on dry deposition capture. Intriguingly, median Logan NADP wet deposition  $\text{NH}_4^+$  concentrations were approximately twofold greater than our bulk deposition  $\text{NH}_4^+$  ( $0.79$  versus  $0.40 \text{ mg N L}^{-1}$ ); possible contributing mechanisms are discussed in greater detail below.

To reiterate, we found similar annual bulk deposition N concentrations across disparate sites in the urban Salt Lake and agricultural Cache Valleys, which in turn were similar to wet deposition from the Green River NADP site. This pattern contrasts with previous work in California that documented increasing  $\text{NO}_3^-$  deposition with proximity to urban versus agricultural emission sources [Tulloss and Cadenasso, 2015]. However, our findings were similar to the results of Lohse *et al.* [2008], who found no significant differences in N deposition among wildland and urban sites upwind and downwind of Phoenix, AZ. Here overall similarities in  $\text{NO}_x$  production between the Salt Lake and Cache Valleys, indicated by similar boundary layer  $\text{NO}_x$  concentrations, may have contributed to patterns in bulk deposition  $\text{NO}_3^-$  concentrations among our study sites. Tropospheric  $\text{NO}_x$  typically has a short lifetime (hours) prior to oxidation to  $\text{NO}_3^-$  [Beirle *et al.*, 2011]. Mean  $\text{NO}_2$  concentrations measured 14 and 11 ppb at sites in the Salt Lake and Cache Valleys, respectively, during 2014 (Utah Department of Air Quality; <http://www.airmonitoring.utah.gov/dataarchive/QL2014-NO2.pdf>). The 25th and 75th percentiles of  $\text{NO}_2$  were 5 and 22 ppb for the

**Figure 3.** Inorganic N concentrations in event-based bulk deposition samples from sites in the Salt Lake Valley (blue circles; six sites) and Cache Valley (red circles; five sites) and weekly wet deposition samples from regional NADP sites (green squares; five sites). (a and b) Nitrate and  $\text{NH}_4^+$  are shown, respectively. Samples collected in this study spanned from December 2013 to February 2015. The black lines represent the GAM fits for the Salt Lake and Cache Valley bulk deposition samples, and the grey lines represent the GAM fits for the NADP sites. (c) Daily and (d) weekly cumulative precipitations measured near our Salt Lake and Cache Valley sites are shown.





Salt Lake site and 4 and 16 ppb for the Cache Valley site. The difference in mean  $\text{NO}_2$  concentrations between the valleys (~27% greater in Salt Lake) was very similar to the difference in median bulk deposition  $\text{NO}_3^-$  concentrations between valleys (~26% greater in Salt Lake; Figure 2), despite the fact that these differences were not statistically significant. Also, the greater peak in summertime  $\text{NO}_2$  concentrations at the Salt Lake relative to the Cache Valley sites (indicated by the greater 75th percentile but similar 25th percentile  $\text{NO}_2$  value) may have driven the significant summertime increase in bulk deposition  $\text{NO}_3^-$  at the Salt Lake Valley sites mentioned above.

Bulk deposition  $\text{NH}_4^+$  concentrations also significantly increased during summer according to the temporal function fit by the GAM (Figure 3a) but did not differ between valleys on a seasonal basis. The similarity in bulk  $\text{NH}_4^+$  concentrations between valleys was surprising given the large differences between putative urban and agricultural  $\text{NH}_3$  sources—i.e., the prevalence of feedlots and fertilized agriculture in the Cache Valley, which are thought to dominate  $\text{NH}_3$  emissions at the global scale [Hertel *et al.*, 2012]. A scale mismatch between the location of  $\text{NH}_3$  emission hot spots and our measurement sites may have contributed to this result. For example, the median wet deposition  $\text{NH}_4^+$  concentration at the Logan NADP site ( $0.79 \text{ mg N L}^{-1}$ ) was approximately double that of the median bulk deposition  $\text{NH}_4^+$  concentrations at the other Cache Valley sites we measured in this study ( $0.40 \text{ mg N L}^{-1}$ ), despite their similar median  $\text{NO}_3^-$  concentrations. The Logan NADP site was located within 1 km of several cattle feedlots, whereas the sites that we sampled were farther away (~10 km) from this particular area.

These patterns suggest that local impacts of agricultural  $\text{NH}_3$  emissions on wet deposition  $\text{NH}_4^+$  may be manifested over finer spatial scales (e.g., <10 km) than reflected by valley-scale measurements. Accordingly, the sites we sampled may not have received a strong  $\text{NH}_3$  influence from animal production despite their close proximity to other agricultural sources and the overall dominance of agricultural land use in the Cache Valley. In support of this interpretation, other studies observed declining  $\text{NH}_3$  concentrations or bulk  $\text{NH}_4^+$  deposition fluxes within hundreds of meters of agricultural point sources [Fowler *et al.*, 1998; Fahey *et al.*, 1999]. Previous work in the Cache Valley showed that atmospheric  $\text{NH}_3$  concentrations varied approximately 2.5-fold between rural and urban sites separated by approximately 15 km (R. Martin *et al.*, Utah State University, unpublished data), further implying highly localized emissions. Spatial heterogeneity in atmospheric reactive N was also indicated by high spatial variation in deposition inorganic N concentrations among sites in a given valley for a given storm event. The mean within-valley standard deviations for a given sampling event (total  $n = 119$ ) in either valley were  $0.22 \text{ mg N L}^{-1}$  for  $\text{NH}_4^+$  and  $0.13 \text{ mg N L}^{-1}$  for  $\text{NO}_3^-$  but reached as high as 2.26 and  $0.94 \text{ mg N L}^{-1}$ , respectively. For context, mean  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations measured  $0.48$  and  $0.42 \text{ mg N L}^{-1}$ , respectively.

Finally, in addition to patterns in emissions, the removal of atmospheric reactive N by plants [Davidson and Kinglerlee, 1997; Sparks, 2009] may also have contributed to variability in bulk deposition values and deviation from expected land use trends. In particular, the presence of greater summer canopy cover from the row crops and pasture in the Cache Valley, compared to the smaller street-tree canopy in the Salt Lake Valley sites, may have facilitated greater net plant uptake of  $\text{NH}_3$  and  $\text{NO}_2$  in the former sites. This effect could have a significant impact on atmospheric N concentrations in each airshed, not just in the vicinity of the canopy, given the documented magnitude of foliar N uptake [Sparks, 2009] and a well-mixed atmospheric boundary layer. Disparities in plant canopy cover may have contributed to observed seasonal differences in  $\text{NO}_2$  concentrations and bulk  $\text{NO}_3^-$  deposition between valleys, while partially attenuating agricultural  $\text{NO}_x$  and  $\text{NH}_3$  emissions to the atmosphere.

As with inorganic N, annual bulk deposition DON concentrations were also similar between valleys, with means of  $0.14 \pm 0.04$  and  $0.14 \pm 0.05 \text{ mg N L}^{-1}$  in the Salt Lake and Cache Valley sites, respectively. However, 49% of the samples measured had DON concentrations below the conservative detection limit we adopted here. A global meta-analysis found that DON typically contributed between 17 and 43% (interquartile range) of total precipitation N [Cape *et al.*, 2011]. The data in our present study fell below this range (~13% of total N), lower than these previous estimates. Thus, we found no evidence that anthropogenic emissions from these valleys increased DON contributions to bulk deposition. If anything, background DON contributions may have been diluted by inorganic N from regional anthropogenic emissions.

### 3.2. Wet Versus Dry Contributions to Bulk N Deposition

The Salt Lake and Cache Valley bulk deposition data showed a greater proportion of extreme  $\text{NO}_3^-$  and  $\text{NH}_4^+$  and concentration values that were  $\geq 1.5$  times the interquartile range (denoted in Figure 2 as circles) as compared with the NADP data, indicative of dry deposition inputs. Significant temporal differences in  $\text{NO}_3^-$  concentrations between the Salt Lake/Cache Valley bulk deposition samples and the NADP wet deposition samples were reflected by trends in the GAM smooth functions, which showed two large peaks in June/July and October/November in our bulk deposition samples relative to the NADP samples (Figure 3). These high values, especially for  $\text{NO}_3^-$ , implied the importance of increased summertime dry deposition in both valleys that was not captured by the NADP wet deposition sampling. The significant difference in summertime  $\text{NO}_3^-$  concentrations between valleys (described above) may have been driven by increased dry deposition in the Salt Lake Valley sites, which showed a pronounced  $\text{NO}_3^-$  peak in June and July. In polluted Southern California airsheds with highly seasonal precipitation inputs, dry deposition to forested canopies represents a dominant form of N inputs [Bytnerowicz and Fenn, 1996; Fenn and Bytnerowicz, 1997; Fenn and Poth, 2004]. In our study area, the temporal distribution of precipitation is more uniform (Figure 3), and significant dry  $\text{NO}_3^-$  deposition to the funnel collector surfaces was only apparent sporadically during summer and late fall.

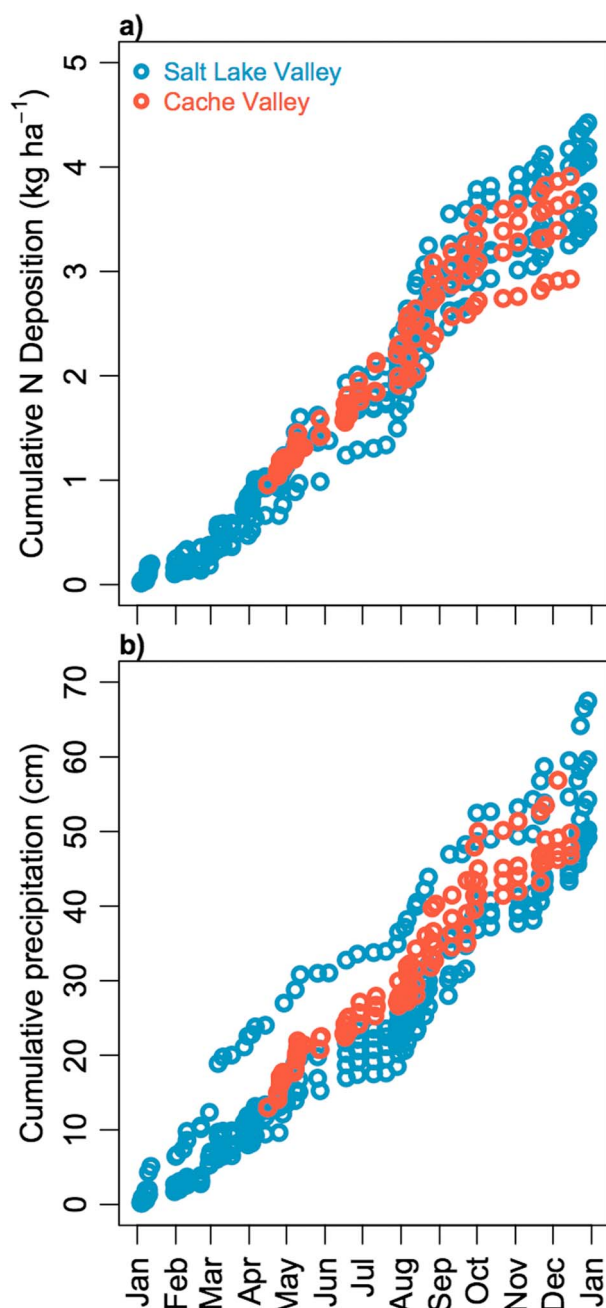
Intriguingly, winter  $\text{NO}_3^-$  concentrations were statistically similar between the bulk deposition data obtained in this study and wet deposition data for the remote NADP sites. This suggests that little winter  $\text{NO}_3^-$  dry deposition was associated with local atmospheric reactive N emissions from the Salt Lake and Cache Valleys, despite the high concentrations of  $\text{NO}_3^-$ -rich  $\text{PM}_{2.5}$  aerosols in these valleys [Mangelson et al., 1997; Kelly et al., 2013]. Previous work in the Salt Lake Valley showed that dry deposition of N to snow was highly variable in space and time [Hall et al., 2014]. Dry deposition increased during periods of persistent cold air pools, and dry deposition N inputs peaked at midelevation montane sites as opposed to the valley floor [Hall et al., 2014], where most of the sites sampled in the present study were located. Our present data provide additional evidence that winter dry N deposition may be spatially limited or sporadic in the study area.

In contrast to the temporal patterns in  $\text{NO}_3^-$  concentrations, summer  $\text{NH}_4^+$  concentrations were similar between the Salt Lake/Cache Valley sites and the regional NADP sites (Figure 3). However, they diverged in winter, when the Salt Lake and Cache Valley samples had slightly but significantly greater  $\text{NH}_4^+$  (note the difference between the GAM fits; Figure 3). This difference may imply a greater and more widespread influence of urban and agricultural  $\text{NH}_3$  emissions on  $\text{NH}_4^+$  deposition during winter, possibly due to seasonal variation in atmospheric conditions. Stable atmospheric conditions often prevail in montane valleys in the intermountain western United States during winter [Lareau et al., 2013], perhaps leading to increased atmospheric  $\text{NH}_x$  concentrations and  $\text{NH}_4^+$  deposition relative to wildland areas.

### 3.3. Bulk N Deposition Totals

Cumulative bulk N deposition was similar between valleys but was variable among sites, ranging between 3.5 and 5.1  $\text{kg N ha}^{-1} \text{yr}^{-1}$  (Figure 4). Bulk deposition rates peaked in July and August, and scaled relatively closely with cumulative precipitation amount, indicating a lack of strong seasonal variation in N inputs (Figure 4). These N deposition rates are modest compared with sites impacted by urban emissions from Los Angeles, CA:  $\sim 30\text{--}90 \text{ kg N ha}^{-1} \text{yr}^{-1}$ , measured using throughfall deposition under forested canopies [Fenn et al., 2003]. However, cumulative N deposition in our study equaled or exceeded measurements and estimates from many remote wildland sites in the western United States ( $\sim 1\text{--}4 \text{ kg N ha}^{-1} \text{yr}^{-1}$ ) [Williams and Tonnessen, 2000; Baron et al., 2011] and was comparable to wet + dry deposition measurements from the Phoenix, AZ, metropolitan area [Lohse et al., 2008]. The bulk N deposition totals we measured here were similar to modeled wet deposition estimates for our study region ( $4\text{--}6 \text{ kg N ha}^{-1} \text{yr}^{-1}$ ) from 2011 to 2013, derived by combining sparse measurements with an atmospheric model [Schwede and Lear, 2014]. Our data suggest that local differences in urban versus agricultural land use do not necessarily affect these regional wet-deposition estimates. However, if N deposition was greater at our valley sites proximate to emission sources as compared with more remote montane areas in the region (i.e., tens of kilometers away [Hall et al., 2014]), our data suggest that this current model might overestimate wet deposition.

Although we saw significant evidence for summer dry deposition  $\text{NO}_3^-$  inputs as described above, our data did not reflect the very high dry deposition N inputs modeled for this region ( $> 12 \text{ kg N ha}^{-1} \text{yr}^{-1}$ ; NADP total



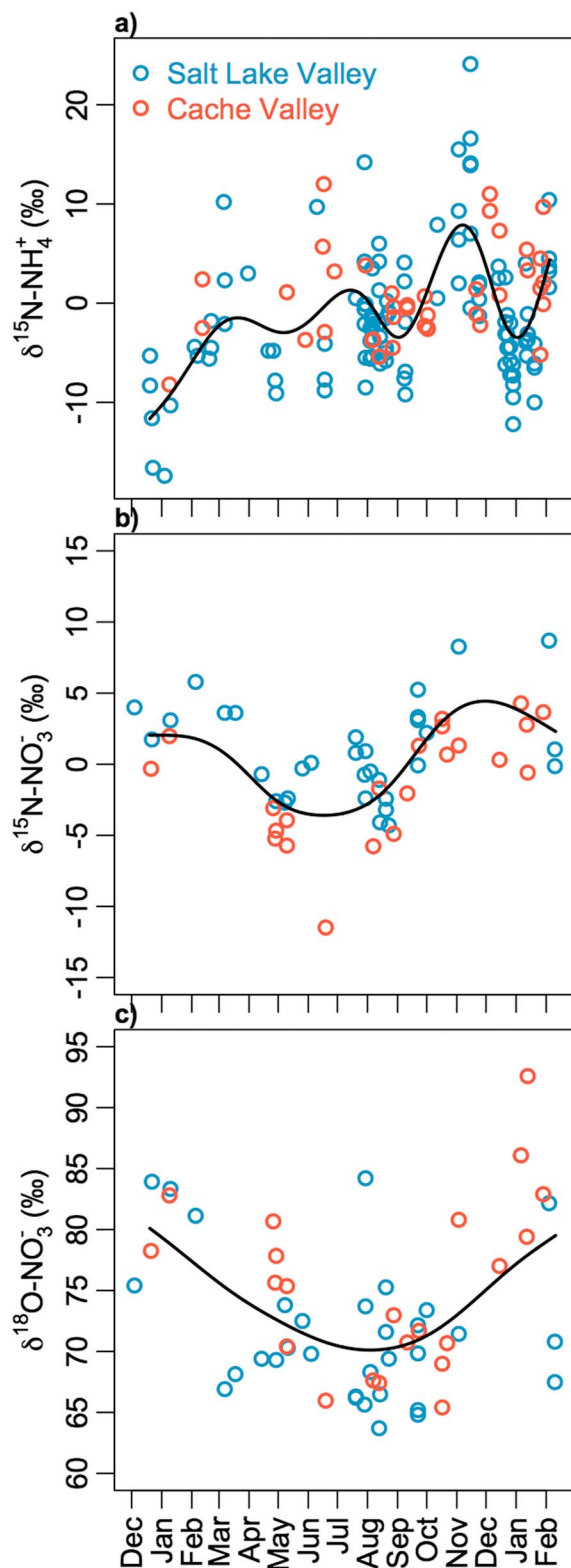
**Figure 4.** (a) Cumulative N deposition and (b) precipitation measured during 2014 at sites in the Salt Lake Valley (blue circles; six sites) and Cache Valley (red circles; five sites).

1 mg NL<sup>-1</sup>, respectively). This variability is indicated by the vertical distance among points of the same color on a given sampling date in Figure 5. This temporal variability is consistent with fine-scale spatial heterogeneity in NH<sub>3</sub> sources as discussed above and variable contributions of particulate N (as discussed below). It also likely reflects spatial and temporal variations in isotope fractionation during scavenging of NH<sub>x</sub> from the atmosphere over the course of precipitation events [Heaton, 1987; Heaton et al., 1997; Xiao et al., 2012], which can function analogous to a Rayleigh distillation. Biogenic NH<sub>3</sub> is typically thought to have lower  $\delta^{15}\text{N}$  values than fossil fuel NH<sub>3</sub>, but few measurements have constrained this variation. Importantly,  $\delta^{15}\text{N}$  values of these sources potentially overlap [Frank et al., 2004; Skinner et al., 2006; Felix et al., 2013]. This source

deposition maps; [http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/preview.aspx#n\\_wd](http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/preview.aspx#n_wd)). This discrepancy likely reflects the fact that the HDPE funnel collectors used here conservatively sampled dry deposition relative to other more complex natural surfaces but also suggests that the model may have overestimated the total area-weighted dry deposition for this region, which has highly variable canopy cover that changes with season, land use type, and landscape position (valley versus montane). Multilayered plant canopies likely would have scavenged much more dry N deposition from the atmosphere than our funnel collectors [Fenn and Poth, 2004; Sparks, 2009], but we suggest that our bulk deposition estimates provide a useful metric for assessing total deposition to the monolayered surfaces—bare soil, rock, pavement, and rooftops—that represent a substantial portion of urban, agricultural, and wildland landscapes in our semiarid study region during much of the year.

#### 3.4. Stable Isotope Composition of Inorganic N Deposition and PM<sub>2.5</sub>

Contrary to our hypothesis that differences in biogenic and fossil fuel reactive N sources would be reflected in N isotope compositions in the Salt Lake and Cache Valleys, we found no significant differences in  $\delta^{15}\text{N}$  values between valleys for either bulk deposition NH<sub>4</sub><sup>+</sup> (Figure 5a) or PM<sub>2.5</sub> (discussed below). Bulk deposition  $\delta^{15}\text{N}$  of NH<sub>4</sub><sup>+</sup> varied widely, between  $-17.4$  and  $24.1\text{‰}$  (mean =  $-0.8 \pm 0.5\text{‰}$ ), but showed no consistent seasonal trend according to the GAM smooth function of  $\delta^{15}\text{N}$  values over time (Figure 5a). We occasionally observed extremely high variability in  $\delta^{15}\text{N}$  of NH<sub>4</sub><sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentrations among sites within a valley during a single storm event (exceeding 10‰ and



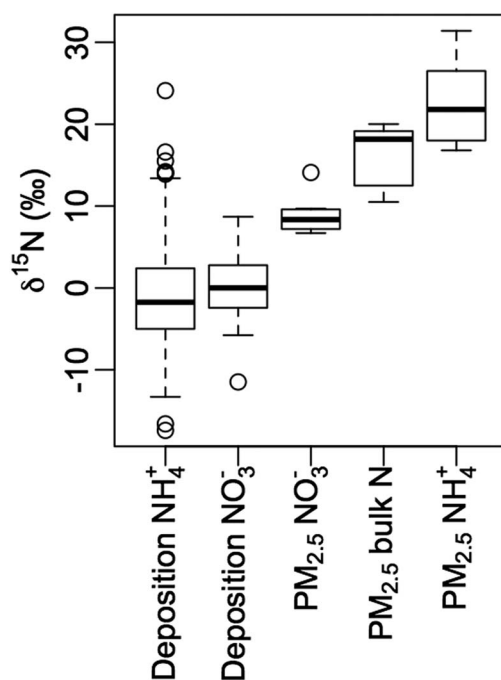
**Figure 5.** Values of  $\delta^{15}\text{N}$  in (a)  $\text{NH}_4^+$  and (b and c)  $\text{NO}_3^-$  in a subset of precipitation samples from the Salt Lake Valley (blue circles) and Cache Valley (red circles).

variability, along with the spatial heterogeneity of biogenic  $\text{NH}_3$  emissions and highly localized deposition described above, may have obscured isotopic differences between valleys despite their probable differences in  $\text{NH}_3$  sources.

In contrast to  $\text{NH}_4^+$ ,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  differed between valleys on a seasonal basis (Figure 5b). Values of  $^{15}\text{N}$  of  $\text{NO}_3^-$  in bulk deposition were significantly lower ( $p < 0.01$ ) in the Cache Valley ( $-4.5 \pm 0.8\text{‰}$ ) than in the Salt Lake Valley ( $-1.3 \pm 0.5\text{‰}$ ) during the growing season (April–October) as assessed with ANOVA, despite the fact that a single GAM function for both valleys adequately described the overall annual trend. This summertime decrease is consistent with an increased summertime biogenic  $\text{NO}_x$  contribution from fertilized Cache Valley agricultural soils, as  $\text{NO}_x$  derived from soil microbes tends to have lower  $\delta^{15}\text{N}$  values than most fossil fuel sources [Li and Wang, 2008; Walters *et al.*, 2015]. On an annual basis,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  measured  $0.0 \pm 0.5\text{‰}$  and was statistically equivalent between valleys. Considering both valleys together,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  showed a significant seasonal trend (indicated by the GAM fit) with lower values during the growing season (Figure 5b). Freyer [1991] found a similar  $\sim 5\text{‰}$  summertime decline in  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in European precipitation and speculated that temperature-dependent isotope exchange reactions among atmospheric  $\text{NO}_y$  species and decreased contributions of particulate  $\text{NO}_3^-$  could also be responsible for seasonal patterns in  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$ , in addition to potential changes in  $\text{NO}_x$  sources. Values of  $\delta^{18}\text{O}$  in bulk deposition  $\text{NO}_3^-$  varied between 63.7 and 92.6‰ (mean  $73.2 \pm 0.9\text{‰}$ ) and also displayed a significant seasonal trend of lower values during the growing season (Figure 5c). This pattern is consistent with seasonal variation in atmospheric  $\text{HNO}_3$  formation pathways [Michalski *et al.*, 2003] and does not necessarily imply variation in  $\text{NO}_x$  sources to the atmosphere.

Mean  $\delta^{15}\text{N}$  values in bulk  $\text{PM}_{2.5}$  ( $15.6 \pm 1.4\text{‰}$ ) and the  $\text{NO}_3^-$  ( $8.8 \pm 0.7\text{‰}$ ) and  $\text{NH}_4^+$  ( $22.5 \pm 1.7\text{‰}$ ) components of  $\text{PM}_{2.5}$  were significantly greater ( $p < 0.0001$ ) than bulk deposition  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  and  $\text{NH}_4^+$





**Figure 6.** Boxplots comparing  $\delta^{15}\text{N}$  values in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  of bulk deposition and  $\text{PM}_{2.5}$ . Bulk N of  $\text{PM}_{2.5}$  represents the total N pool.

with the most enriched values of  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in bulk deposition (Figure 6). The bulk deposition  $\delta^{15}\text{N}$  values  $>10\text{‰}$  exceed most previous wet deposition measurements [Heaton, 1987; Fukuzaki and Hayasaka, 2009; Jia and Chen, 2010; Xiao et al., 2012]. Concentrations of the ammonium sulfate portion of  $\text{PM}_{2.5}$  remain relatively consistent throughout the year in our study area, despite the fact that ammonium nitrate and total  $\text{PM}_{2.5}$  mass increase during winter [Hand et al., 2012]. Thus, one plausible interpretation of the occasionally high values of  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  observed in bulk deposition (Figure 6) was that they reflected an increasing contribution of particulate  $\text{NH}_4^+$  (i.e.,  $\text{NH}_4^+$  derived from  $\text{PM}_{2.5}$  or larger aerosols), in addition to potential variation in sources. Importantly,  $\delta^{15}\text{N}$  values of bulk deposition  $\text{NH}_4^+$  frequently exceeded  $0\text{‰}$ , greater than many previous estimates of  $\delta^{15}\text{N}$  values for biogenic or fossil fuel  $\text{NH}_3$  sources described above. A variable contribution of  $\delta^{15}\text{N}$ -enriched particulates thus provides a plausible explanation for sporadically high  $\delta^{15}\text{N}$  values of deposition  $\text{NH}_4^+$ , an interpretation that appears to have received little attention in the literature.

This interpretation is bolstered by contrasting our results with wet deposition  $\delta^{15}\text{N}$  data from China, Japan, and South Africa [Heaton, 1987; Fukuzaki and Hayasaka, 2009; Jia and Chen, 2010; Xiao et al., 2012]. These studies consistently found  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  values  $<0\text{‰}$  for precipitation samples with no dry deposition component. These studies were also located in areas impacted by mixtures of urban and agricultural  $\text{NH}_3$  sources, as were our study sites; consequently, the large positive  $\delta^{15}\text{N}$  deviations we observed in some samples could be parsimoniously explained by a variable contribution of dry particulate  $\text{NH}_4^+$  deposition collected in our bulk samplers, which was not sampled in these wet deposition studies. Similarly, values of  $\delta^{15}\text{N}$  in bulk deposition  $\text{NO}_3^-$  occasionally reached as high as  $8.7\text{‰}$ , similar to the mean values in  $\text{PM}_{2.5}$  ( $8.8 \pm 0.7\text{‰}$ ; Figure 6). Therefore, our bulk deposition  $\text{NO}_3^-$   $\delta^{15}\text{N}$  values could also potentially be interpreted as a variable mixture of  $\delta^{15}\text{N}$ -enriched particulate  $\text{NO}_3^-$  and  $\delta^{15}\text{N}$ -depleted gaseous  $\text{HNO}_3$ , in addition to a mixture of isotopically variable  $\text{NO}_3^-$  sources as discussed above.

Overall, the mass- and volume-weighted isotopic compositions and standard errors of  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in bulk deposition measured  $-1.6 \pm 0.4$  and  $0.8 \pm 0.5\text{‰}$ , respectively. Given that volume-weighted mean concentrations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  measured  $0.34 \pm 0.01$  and  $0.24 \pm 0.01 \text{ mg NL}^{-1}$ , respectively, weighted  $\delta^{15}\text{N}$  of total inorganic N measured  $-0.6 \pm 0.7\text{‰}$ . Because relatively few comprehensive studies of the isotope composition of bulk N deposition have been conducted, these measurements provide a useful

(Figure 6). The  $\text{NH}_4^+$  component of  $\text{PM}_{2.5}$  had especially high  $\delta^{15}\text{N}$  values. These measured  $24.1 \pm 2.3$  and  $20.1 \pm 1.6\text{‰}$  in the Salt Lake and Cache Valley sites, respectively, but differences were not statistically significant. Values of  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  were much lower than  $\text{NH}_4^+$  of  $\text{PM}_{2.5}$  but were still significantly greater than  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  observed in bulk deposition (Figure 6). In the Salt Lake and Cache Valleys,  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  measured  $9.5 \pm 1.0$  and  $7.7 \pm 0.5$ , respectively, and did not significantly differ. Values of  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$  of  $\text{PM}_{2.5}$  measured  $81.6 \pm 2.7\text{‰}$ , similar to bulk deposition. Annual mean concentrations of  $\text{PM}_{2.5}$  were similar at monitoring sites in both study valleys during 2013 and 2014 (Utah Department of Air Quality; <http://www.airmonitoring.utah.gov/dataarchive/>).

The high  $\delta^{15}\text{N}$  values of  $\text{PM}_{2.5}$  are consistent with an  $\sim 33\text{‰}$  equilibrium fractionation between gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  and  $\sim 21\text{‰}$  for ammonium nitrate relative to nitric acid vapor [Heaton et al., 1997]. These fractionations lead to much greater  $\delta^{15}\text{N}$  in  $\text{PM}_{2.5}$  relative to gaseous precursors. Individual  $\text{PM}_{2.5}$  samples varied between  $17.3$  and  $31.4\text{‰}$  in  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and overlapped

constraint for ecosystem-scale N isotope models. For example, N isotope mass balance has been used to estimate the importance of denitrification at the global scale, requiring an estimate of the N isotope composition of atmospheric deposition inputs [Houlton and Bai, 2009]. It is uncertain whether concentrated urban or agricultural N emissions might alter the isotope composition of deposition measured in more remote ecosystems. Previous studies in natural ecosystems had a median  $\delta^{15}\text{N}$  value of  $-1.3\text{‰}$  [Houlton and Bai, 2009], similar to our present data. These similarities imply that local urban or agricultural influences do not necessarily impart a significant isotopic signature to bulk deposition N inputs on an annual basis.

#### 4. Conclusions

Despite the strong impacts of land use on  $\text{NO}_x$  and  $\text{NH}_3$  emissions documented elsewhere [Galloway et al., 2004; Hertel et al., 2012], we conclude that substantial valley-scale differences in urban versus agricultural land use in northern Utah were not strongly manifested in the mean speciation, isotope composition, or fluxes of bulk atmospheric N deposition to our funnel collectors on an annual basis. Differences between valleys were only apparent during summer, when bulk deposition  $\text{NO}_3^-$  concentrations increased at the Salt Lake Valley sites, and  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  was lower at the Cache Valley sites. Our data suggest that relatively coarse regional estimates of these parameters may suffice for use in ecosystem-scale N cycling models, although they may miss hot spots of  $\text{NH}_3$  emissions that are deposited very close to the source. Although median-measured bulk deposition N concentrations exceeded wet deposition concentrations from several remote NADP sites in the region, they were similar to wet deposition from another regional NADP site. It is well known that plant canopies scavenge gaseous and particulate reactive N to a greater extent than the funnels we used to collect bulk deposition [Fenn and Poth, 2004; Sparks, 2009; Bettez and Groffman, 2013]. However, our bulk deposition estimates likely provide a useful metric for estimating total deposition to nonvegetated surfaces—soil, rocks, pavement, and rooftops—that represent a substantial portion of wildland, urban, and agricultural landscapes in the intermountain western United States, especially during fall and winter.

Values of  $\delta^{15}\text{N}$  in atmospheric deposition are complex to interpret because they not only represent a mixture of reactive N sources varying in  $\delta^{15}\text{N}$  but also a variable mixture of phases (gas, particulate, and aqueous) impacted by large isotope fractionations. Our data highlight the potential importance of the latter phenomenon. We found large differences between  $\delta^{15}\text{N}$  of bulk deposition and  $\text{PM}_{2.5}$ , suggesting that temporal variation in particulate contributions to bulk N deposition could potentially obscure initial isotope differences among biological versus fossil fuel reactive N sources. Even where source  $\delta^{15}\text{N}$  values differ, spatial and temporal heterogeneities in particulate contributions could decrease the power to detect these differences. Thus, we recommend caution when interpreting atmospheric  $\delta^{15}\text{N}$  measurements solely in terms of mixtures of sources. This is especially important when sampling schemes may selectively capture gaseous versus particulate N as opposed to the entire atmospheric reactive N pool, thus leading to physical isotope fractionation.

#### Acknowledgments

Upon manuscript acceptance all data are publicly available online at the Hydroshare database: <http://dx.doi.org/10.4211/hs.7ce47150ee344-d4e95f2fd7bb4f660ac>. We thank four anonymous reviewers for their thoughtful comments and the NADP program for providing their data online. S. Chakraborty and D. Fernandez provided the analytical assistance and D. Eiriksson, E. Schulze, D. Tarboton, B. Greene, D. Epstein, S. Jackson, J. Turner, A. Armstrong, and H. Quinn assisted with sample collection. J. Wessling, D. Zhang, and X. Xu contributed to sample analysis. We also thank Utah Department of Air Quality staff, especially S. Arens, for assistance with  $\text{PM}_{2.5}$  collection and B. Schichtel from the U.S. National Park Service for use of a high-volume sampler. This research was supported by National Science Foundation (NSF) EPSCoR grant IIA 1208732 awarded to Utah State University as part of the State of Utah Research Infrastructure Improvement Award and by NSF grant DBI-1337947 to the University of Utah. Any opinions, findings, and conclusions or recommendations expressed are those of the author (s) and do not necessarily reflect the views of the National Science Foundation.

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